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Hydraulic and Mineralogical Characterization of Organoclay Before and After Reaction with Non-Aqueous Phase Liquid (NAPL)

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HYDRAULIC AND MINERALOGICAL CHARACTERIZATION OF ORGANOCLAY BEFORE AND AFTER REACTION WITH NON-AQUEOUS PHASE LIQUID (NAPL)

by

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ABSTRACT

Sediment capping—a method used to stabilize and remediate contaminated subaqueous sediment in lakes or river shores by covering the contaminant with multiple layered materials— is a more effective, economic, and durable in situ treatment compared to ex situ methods such as dredging. The caps are typically composed of porous geo-materials such as gravels, sands, Reactive Core Mat (RCM), including reactive soils (e.g., organoclay) and geosynthetics (e.g., geotextiles). The designed caps are regarded as water-permeable so as not to disturb the sediment; however, the caps become unsaturated state because of trapped gas generated from the decomposition of organic matter. Most of the past studies have emphasized only permeability when it is saturated; however, the contaminant transport aspect of the RCM and the mechanical integrity of this cover system under unsaturated condition has not been studied. In this study, to manage coal-tar creosote, a non-aqueous-phase liquid (NAPL) consisting primarily of polynuclear aromatic hydrocarbons (PAHs), the unsaturated hydraulic properties of organoclay was investigated. The water retention properties of organoclay before and after contact with NAPL by using unsaturated soil testing apparatus were experimentally evaluated. The data was modeled and analyzed by using van Genuchten (vG) and Brook-Corey (BC) fitting models. Furthermore, the mineralogical properties measured by X-Ray Diffraction (XRD) were analyzed with water retention properties. The higher the air entry (Ψ_A) the lower the hydraulic conductivity and permeability of the sample. The hydraulic conductivity drops dramatically as air enters the samples with the unleaded gasoline organoclay sample exhibiting the lowest permeability. The unsaturated hydraulic conductivity obtained from the vG and BC models are far apart (magnitude of 10^6) and the reason is the pore interaction parameters not being suitable for organoclay. The trend of fitting parameters and smectite content and therefore degree of reaction, demonstrate unsaturated properties changing from coarse to finer WRC behavior. The results can be used in later studies to address the effects of bulging on the performance of RCM and the need to protect against this phenomenon in the sediment capping system.

1. INTRODUCTION

Contaminated aquatic sediments are one of the most widespread and serious environmental problems faced by both developed and developing countries. For instance, 581 out of 1,290 Superfund sites in the United States contain contaminated sediments (U.S. EPA 2011a) and 11 of these 581 sites are known as mega sites, that is, those estimated to cost more than 50 million dollars per site to remediate. Polycyclic aromatic hydrocarbons (PAHs) and Polychlorinated biphenyl (PCBs), are the primary risk factors at more than one-fifth of the contaminated sediment sites (U.S. EPA 2011b). These sediments pose ongoing risks to aquatic ecosystems and humans via the food chain.

Polynuclear aromatic hydrocarbons (PAHs), a group of nonionic hydrophobic organic compounds (HOCs), generally constitute 50% or more of Creosote and typically are the driver for remediation at wood-treating facilities. PAHs are an environmental concern because of their toxicity and potential carcinogenicity (van der Oost et al. 2003; Jonker et al. 2006; Qu et al. 2008; Lee e t al. 2012). There are three major types of PAH sources: pyrogenic PAHs that are emitted during incomplete burning of coal, oil, gas, coke, wood, garbage, or other organic material; petrogenic PAHs that form in the earth by geological processes at low temperature, possibly high pressure and over long time periods that are the basis for crude oil, coal, coal tar pitch, and asphalts; and diagenetic PAHs that are derived from biogenic precursors like plant terpenes in sediments (Crane et al., 2010).

Creosote is a representative non-aqueous phase liquid (NAPL) that is slightly denser than water. NAPLs are liquid solution contaminants that do not dissolve in or easily mix with water (hydrophobic), like oil, gasoline and petroleum products. NAPLs tend

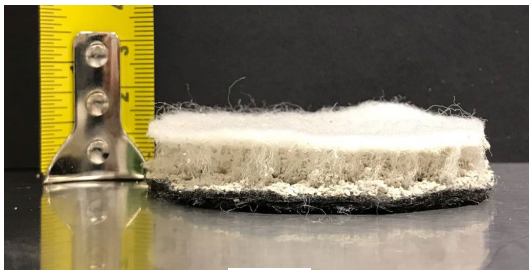
to contaminate soil and groundwaters. Many common groundwater contaminants such as chlorinated solvents and many petroleum products enter the subsurface in nonaqueous-phase solutions. They do not mix readily with water and therefore flow separately from ground water. When released to the subsurface, creosote commonly resides below the groundwater table but may not fall to an aquitard, confining layer, or similar layer with finer texture. Stringers of creosote can form where subtle transitions in texture occur and migrate in the general direction of groundwater flow. Creosote from a railroad tie-treating facility can form stringers below the groundwater table that migrated toward a nearby lake. NAPL flowed into the lake, resulting in an “organic sheen” on the water surface. As a part of NAPL, PAHs dissolved in groundwater adjacent to the stringers also migrated into the lake, further degrading water quality.

One of the recent superfund sites is located at Fox River located in northeastern Wisconsin, USA. The Lower Fox River, begins at the Menasha and Neenah channels leading from Lake Winnebago and flows northeast for 39 miles where it discharges into Green Bay and Lake Michigan. Approximately 270,000 people live in the communities along the river. The river has 12 dams and includes the highest concentration of pulp and paper mills in the world. During the 1950s and 1960s, these mills routinely used PCBs in their operations which ultimately contaminated the river. PCBs do not degrade naturally, but instead concentrate in the environment and the food chain resulting in health hazards to people, fish and wildlife. When the cleanup is completed in August, it will have addressed more than 6 million cubic yards of PCB-contaminated sediment across 39 miles of the Lower Fox River, at an estimated cost of $1 billion. Work has been ongoing since 2004 by the companies determined to be responsible for the contamination. (EPA report on FOX river superfund site)

Dredging and capping in the river was necessary there after contractors collected samples north, south and at the confluence of the East and Fox Rivers in 2017 to determine the extent of tar-like material found there. This tar-like material, consisting of PAHs, was the result of manufactured gas plant processes that operated in the area in the early 1900s. The remediation techniques used at this superfund site consisted mainly of dredging and then sand and gravel capping to reduce the transport of any residual contamination from the riverbed. Dredging is one of the traditional and extremely costly remediation methods due to the transport and final treatment of the sediments. As an alternative, thin reactive capping systems are newly developed techniques that contain the contamination and are considerably cost effective (Locate et al. 2003; Reible et al. 2003, 2006; Yuan et al. 2009; Olsta 2010; Perelo 2010; Eun et al. 2012a,b; Ebrahimi et al. 2014, 2016; Zhang et al. 2016; Gu et al. 2017). Since 1990, about six million square meters of contaminated sediment have been removed and disposed of through the implementation of 71 major environmental remediation projects in the United States (Zeller and Cushing 2006). The caps are typically composed of porous geo-materials such as gravels, sands, reactive soils, and geosynthetics (e.g., geotextiles). The designed caps are regarded as water-permeable so as not to disturb the sediment.

Reactive Core Mat (RCM) represents a class of *in situ* sediment remediation technique, consisting of a reactive layer containing one or more neutralizing or otherwise reactive materials (e.g., organoclay, apatite, activated carbon) confined between two permeable geotextile filtering layers (Fig. 01). The 1.00 cm thick RCM is placed on the sediment and approximately 10 - 20 cm of overlying soil is placed on the RCM for stability and protection. Installed as an active in situ treatment layer directly over contaminated sediment, RCM can be deployed instead of dredging (Fig. 02). Depending on site

conditions, traditional sand caps may prove unfeasible, or result in an excessively thick design.



(a)

(b)

(c)

Figure 01: (a) side view of Reactive Core Mat (RCM). (b) top geotextile (c) bottom geotextile

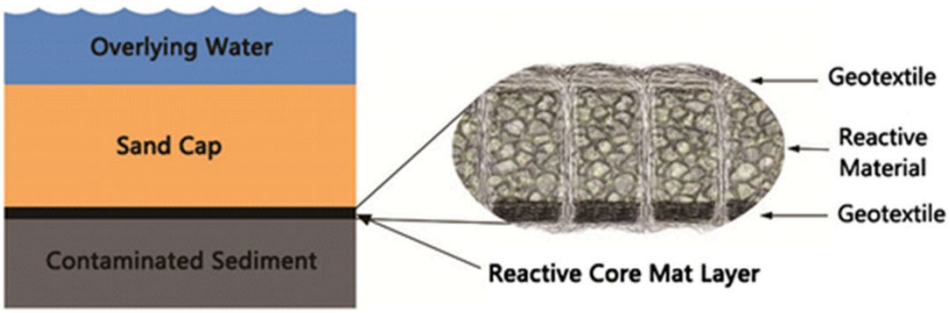


Figure 02: RCM are placed on top of the contaminated sediment and covered with a thin sand cap to protect against erosion and to keep the RCM in place. The capping using this method is much thinner than traditional caps and cost effective compared to dredging.

One developing concern regarding RCM layers is a bulging effect caused by methane accumulation beneath the cover. Methane gas is generated inside NAPL contaminated sediments. After reaction the organoclay section of RCM layers become impermeable and brittle. Sufficient pressure underneath the RCM will lead to its mechanical failure and will no longer effectively contain the contaminants. For this reason, a three-stage study was designed to study and observe the bulging effect on RCM cover systems (Mohan et al. 2000; Alshawabkeh et al. 2005; McLinn and Stolzenburg 2009a, b; Chattopadhyay et al. 2010). Stage one (1) is to characterize hydraulic and mineralogical properties of organoclay before and after contamination with fuels and organic liquids which is the contents of this thesis. Stage two (2) consists of testing the bulging effect in a lab scale column designed for this purpose to observe and evaluate the RCM's mechanical failure and contaminant transport through the cover. Stage three (3) consists of numeric modeling of the mechanical failure and contaminant inside the testing column.

Organoclay's hydraulic properties after NAPL contamination have been studied by other researchers (Lee et al. 2012 and Benson 2015). Most of the past studies have emphasized only permeability in the saturated condition; however, the contaminant transport aspect of RCM and the mechanical integrity of this cover system under the unsaturated condition has not been studied. To manage coal-tar creosote, a non-aqueous-phase liquid (NAPL) consisting primarily of polynuclear aromatic hydrocarbons (PAHs), the unsaturated hydraulic properties of organoclay was investigated in this study. This study experimentally evaluated the water retention properties of organoclay before and after contact with NAPL by using unsaturated soil testing apparatus. Furthermore, the mineralogical properties measured by XRD were correlated with water retention properties. Thus, the relationship between the degree of

reaction and change of water retention in the organoclay was investigated. The results can be used in later studies to address the effects of bulging on the performance of RCM and the need to protect against this phenomenon in the sediment capping system.

2. MATERIALS

2.1. Organoclays

Organoclays are modified clays in which the hydrophilic mineral surface has been transformed to an organophilic and hydrophobic surface by replacing the cations natively bound to the mineral surface with organocations. The organoclay and the RCM used in these tests is manufactured and provided by CETCO, Minerals Technologies (Minneapolis, MN). Organoclays commonly are synthesized using sodium (Na) bentonite that has been exchanged with quaternary ammonium cations. Organoclay consists of uniform sand-sized granules of organoclay ranging in size from 2 to 0.25 mm (Fig. 03). Compared to sand, the organoclay shows larger particle size and poorly grading. The C_u of organoclay and sand are 1.4 and 3.0, respectively. The specific gravity of solids is 1.62 (three tests), which is lower than the specific gravity of Na bentonite because of the organic cations bound to the mineral surface (Soule and Burns 2001; Burns et al. 2006; Lee et al. 2012). The results of X-ray diffraction indicate that the bentonite fraction of the organoclay consists of 65% smectite, 13% quartz, 11% plagioclase feldspar, 7% halite, and 3% potassium feldspar. In the presence of organic liquids, organoclays can behave in a manner similar to Na bentonites contacted with water, i.e., exhibiting high plasticity, swelling, and low hydraulic conductivity.

2.2. Fuels and Pure Organic Liquids

Two fuel types were used as saturated contamination to speed up the reaction time for the RCM material to perform the tests before and after complete reaction with NAPLs. NAPLs form from the incomplete combustion of hydrocarbons, such as coal and gasoline. Pure Methanol (CH_3OH) and unleaded gasoline were used for this purpose. Then Methanol, ACS was provided from LabChem (Zelienople, PA), which was stored in the PKI environmental laboratory and the unleaded gasoline was purchased from the nearby gas station. The hydrodynamic properties of these liquids are listed in table 01. (Green and Perry 2007).

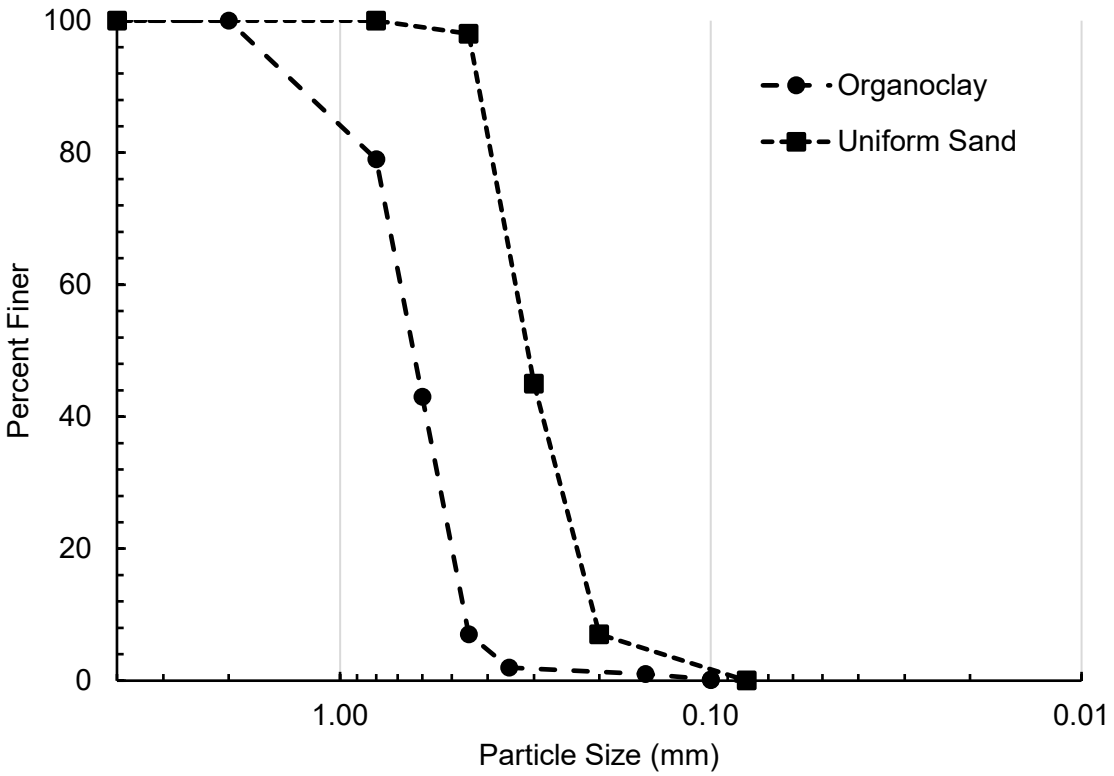


Figure 03: Organoclay sieve analysis

Table 01: Hydrodynamic properties of fuels (Data from Green and Perry 2007)

Liquid	**Density** $(kg/l)\ at\ 20\ ℃$	**Kinetic Viscosity** $(m/s^2)\ \times\ 10^6\ at\ 20\ ℃$	**Log octanol-water partition coefficient**
Unleaded Gasoline	0.80	0.45	3.60 - 8.10
Gasoline	0.78	0.70	-0.90

3. METHODS

3.1. Saturated Hydraulic Conductivity (K_{sat})

To obtain water retention curves of organoclay, the saturated hydraulic conductivity is to be measured. The saturated hydraulic conductivity is performed in accordance with ASTM D5856 using constant head and falling head tests. The transparent cylinders used in this test are 12.7 cm (5 inch) in height and 6.35 cm (2.5 inch) in diameter. The test will be performed on three organoclay specimens, clean organoclay, contaminated with unleaded gasoline and methanol. Clean organoclay has high permeability similar to sand and is tested using the constant head test by filling the entire column with organoclay and then saturating the sample to perform the test. The other two contaminated specimens display a much lower hydraulic conductivity duo to reaction of organoclay with NAPLs thus are tested using the falling head method and only a third of the column is filled with the contaminated organoclay sample and the rest is filled with gravel and the saturated hydraulic conductivity is evaluated using the series layering method (Fig. 04). Each test is performed three times to ensure repeatability of results.

The samples must be contaminated while inside the testing column to preserve the integrity and the structure that is formed after the organoclay is contaminated with unleaded gasoline and methanol. This greatly effects the permeability of the organoclay specimens (up to a factor of 10^2) since contaminated samples are brittle and disturbing the samples before testing results in the formation of pathways that increase permeability.

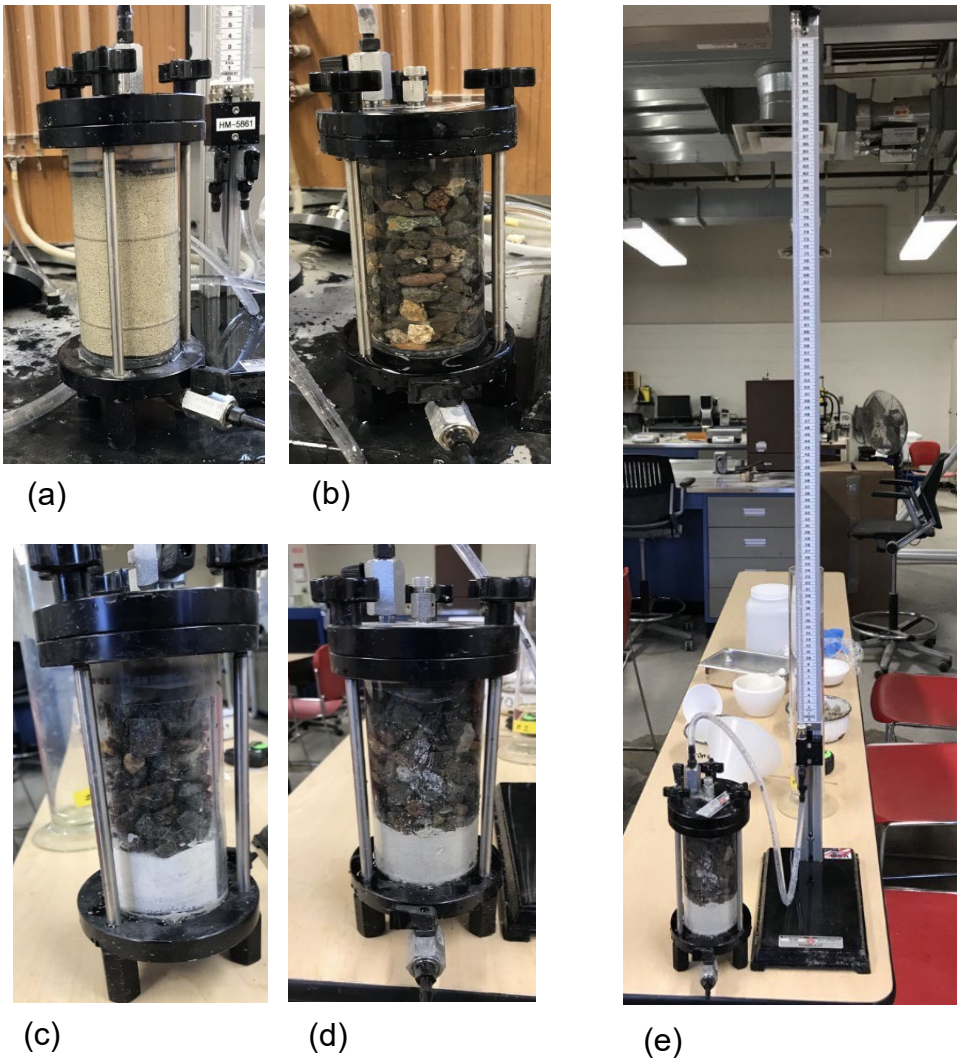


Figure 04: Constant head test setup on (a) clean organoclay and (b) gravel. Falling head tests on (c) and (d) organoclay hydrated with methanol and unleaded gasoline at the bottom of the cylinder filled with gravel. (e) displays the falling head test setup for the specimen (d).

3.2. Water Retention Curve (WRC)

In order to evaluate and compare the effects of NAPL contamination on organoclay's unsaturated hydraulic characteristics, three specimens of organoclay were prepared each time in cylinder shaped plastic molds, 7.5 cm in diameter and 5 cm in height containing 200 grams of organoclay. These molds are designed to be placed inside the hanging column funnel and later on the pressure plate for unsaturated hydraulic testing. One sample is saturated with unleaded gasoline and another with pure methanol and covered to reduce evaporation and placed inside chambers to fully react with the organoclay for 24 hours (Fig. 05). Afterwards the hydrated samples are left to dry out for 24 hours so any remaining liquid fuel evaporates before any further testing can commence. Samples must be saturated with water before testing so they are placed inside saturation chambers under one atmospheric suction for 24 hours. The unsaturated hydraulic conductivity tests are performed in accordance with ASTM D6836. First test is the hanging column for suction values up to 10 kPa where the three samples are placed on top of ceramic plates in funnels which has been previously saturated under one atmospheric suction for 24 hours (Fig. 06). After stabilizing the apparatus, small increments of suction (starting from 0.2 kPa and as high as 1.0 kPa) are applied to the sample by adjusting the water head. The sample is left to equalize for 24 hours before a new suction increment is applied. The volumetric water content (θ) is calculated using the water being sucked out of the sample to achieve the water retention curve ($\theta \; vs \; \varphi$).

To apply suctions higher than 8 kPa, the two contaminated samples are then moved to the pressure plate for suctions up to 250 kPa. The ceramic plate inside the pressure plate is fully saturated inside a chamber subject to one atmospheric suction for 24 hours. Suction increments are applied every 24 hours for the sample to equalize.

In the hanging column test suction is applied from underneath the sample using water head difference while in the pressure plate air pressure is applied from above, pushing water out from underneath. The air entry of the ceramic plates must be higher than the sample themselves that is why fully saturation of the ceramic plate is crucial to the accuracy and reliability of the results. The three samples are tested together, while the clean organoclay is only tested using the hanging column due to its high permeability. This process is repeated three times to ensure repeatability of the results (Series 1, 2 and 3).

3.3. Modeling of Water Retention Curves

Two models the Brooks and Corey (1964) and van Genuchten (1980) were used to fit WRC data. The Brooks-Corey model is more suitable for undisturbed samples and tends to have a poor fit near the saturation and a discontinuous slope of WRC (van Genuchten, 1985) because of the discontinuity of the model, while the van Genuchten equation is a sigmoidal fitting equation (van Genuchten, 1980) and generally provides a better fit. The Fredlund-Xing (1994) model which has proved to be more accurate than others in the past was not used for the organoclay as the mean squared error (MSE) values obtained from this model were high and a proper fit could be attained. The Brooks-Corey equation is presented as:

$$\Theta = \frac{\theta-\theta_r}{\theta_s-\theta_r} = \left(\frac{\psi_a}{\psi}\right)^{\lambda} \quad for \;\; \psi \geq \psi_a \tag{1}$$

$$\Theta = 1 \quad for \;\; \psi < \psi_a$$

where Θ is normalized volumetric water content, θ_r is residual water content, θ_s is saturated water content, ψ_a is air entry suction, and λ is the pore-size distribution index. The van Genuchten model can presented as:

$$\Theta = \left[\frac{1}{1+(\alpha\psi)^n}\right]^m \quad (2)$$

where α, m, and n are empirical parameters found by fitting the van Genuchten equation to the data. The fitting parameter α is approximately equal to the inverse of a ψ_a , or the suction at which the largest pores begin to drain; while the fitting parameter n governs the slope of the line when suction exceeds a ψ_a. m is equal to 1-1/n.

The unsaturated hydraulic conductivity is then attained from WRC data and saturated hydraulic conductivity values using van Genuchten and Brooks and Corey models. The function for k_θ commonly used with Brooks-Corey WRC function (1) is:

$$k_\theta = k_s\Theta^{(2/\lambda+p+2)} \quad (3)$$

where k_θ is the hydraulic conductivity at volumetric water content θ, p is the pore interaction parameter and k_s is the saturated hydraulic conductivity.

The k_θ function commonly used with van Genuchten WRC function (2) is:

$$k_\theta = k_s\Theta^l\left[1-(1-\Theta^{1/m})^m\right]^2 \quad (4)$$

where l is the pore interaction parameter.

The parameters defining Eqs 1 through 4 are related to physical properties of porous media. In the Brook-Corey system, Ψ_a increases in magnitude when the largest pore in the medium is smaller in size (i.e., air-entry suction increases as the maximum pore size decreases). In the same system, λ increases if the pore size distribution of the media is narrow (uniform pore sizes) and decreases if the pore-size distribution of the media is broad (nonuniform pore sizes). In the van Genuchten system, α is inversely related to

the air-entry suction and therefore decreases as the largest pore within the medium decreases in size (i.e., a decreases as the air-entry suction increases). The n parameter in the van Genuchten increases with narrowing pore-size distribution (consistent with λ in the Brooks-Corey). In the k_θ functions (Eqs 3 and 4), the pore interaction terms p (Eq 3) and l (Eq 4) are not known to have a consistent correlation or relationship with any particular physical property of porous media (Schaap and Leij 2000). Thus, these parameters are different for different material. The parameters in the Eqs 1 through 4 are determined by minimizing the mean squared error values for each WRC.

The WRC functions (Eqs 1 and 2) do not include the pore interaction terms (p or l), so these parameters are commonly assigned as $p = 2$ in Eq 3 or $l = 0.5$ in Eq 4 (Brooks and Corey 1966; van Genuchten 1980).

3.4. X-Ray Diffraction

In order to observe the mineralogical changes of organoclay after NAPL contamination, the XRD test was performed at UNL's NanoTech center in Lincoln. Clean organoclay and organoclay samples contaminated with methanol and unleaded gasoline were tested using this method. X-ray diffraction relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials where a beam of incident X-rays diffract into many specific directions.

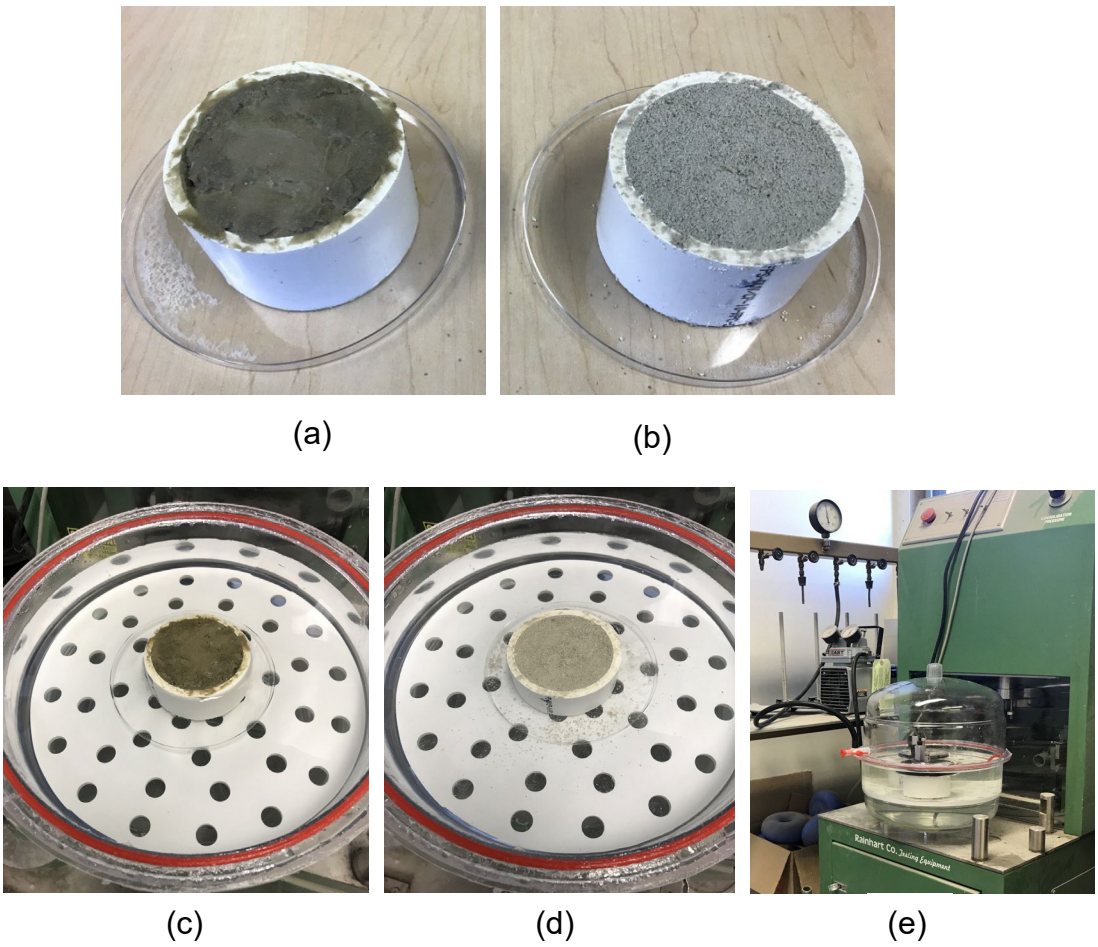


Figure 05: Plastic molds 7.5 cm in diameter and 5 cm in height containing 200 grams of organoclay after contamination with (a) unleaded gasoline and (b) methanol. (c) and (d) display the saturation process inside the saturation chamber for the two contaminated organoclay specimens before unsaturated hydraulic testing. (e) The saturation chamber setup that is used to apply one atmospheric suction to saturated the samples and ceramic plates.

(a)

(b)

(c)

Figure 06: (a) Hanging column test setup able to test on three samples simultaneously for suctions up to 8 kPa. (b) Three organoclay specimens inside the hanging column funnels being during testing (from left to right unleaded gasoline, methanol contaminated and clean organoclay). (c) Pressure plate setup to apply suctions for 8 kPa up to 250 kPa.

4. RESULTS AND DISCUSSIONS

Unleaded gasoline and methanol had quite different reactions on organoclay. From a visual viewpoint, unleaded gasoline reacted very fast compared to methanol in a manner that it proved difficult to contaminate a thick layer of organoclay with gasoline. Top section of organoclay would react so fast when in contact with unleaded gasoline that the rest of the liquid could not penetrate to bottom layers and would remain on top. A mere two centimeters of organoclay after contact with unleaded gasoline would result in an impermeable block of dark grey fine material. For this reason, the thickness of the samples were limited to a few centimeters. The organoclay sample contaminated with methanol did not change color and the grain structure was still visible after reaction while a certain cementation would form between the grains holding it together and reducing the permeability, the integrity and said structure was susceptible to impact and would break if shaken. The organoclay sample contaminated with unleaded gasoline became very hard and brittle but its structure would not lose its integrity as easily.

4.1. Saturated Hydraulic Conductivity of Organoclay Specimens

The intrinsic permeability (k) and hydraulic conductivity (K) of a porous medium are related by (Fernandez and Quigley 1988).

$$K = k\,\frac{g}{\upsilon} \tag{5}$$

where $\upsilon =$ kinematic viscosity of the permeant liquid; and $g =$ gravitational acceleration. The intrinsic permeability reflects the influence of the geometry of the pore space (i.e., size, shape, and connectivity of the pores) on the rate of fluid flow through a porous material, whereas the hydraulic conductivity accounts for the

geometry of the pore space and the hydrodynamic properties of the fluid flowing in the pores (v). Liquids that alter the intrinsic permeability alter the pore network in a soil (Fernandez and Quigley 1988). For organoclays, the alteration is caused by swelling as the organoclay solvates in the same manner that occurs when a Na bentonite is hydrated during permeation with water (Lee et al. 2012).

The saturated hydraulic conductivity of organoclay specimens are shown in Fig. 07 and Table 02. The hydraulic conductivity of clean organoclay is very high ($3.0 \times 10^{-1}\ cm/s$) and in this state is not effective in containing any contaminant. After reaction with NAPL the permeability drops to $8.8 \times 10^{-4}\ cm/s$ for the methanol organoclay sample and $2.3 \times 10^{-7}\ cm/s$ for the unleaded gasoline organoclay sample, respectively 10^3 and 10^6 times smaller than before contact. The reduction in permeability of organoclay would make it impermeable against NAPL contaminated sediments.

Table 02: Saturated hydraulic conductivity of organoclay specimens obtained from constant head and falling head tests.

Specimen	**Saturated Hydraulic Conductivity (cm/s)**
Clean Organoclay	3.0×10^{-1}
OC + Methanol	8.8×10^{-4}
OC + Methanol (Benson 2014)	1.1×10^{-3}
OC + Gasoline	2.3×10^{-7}

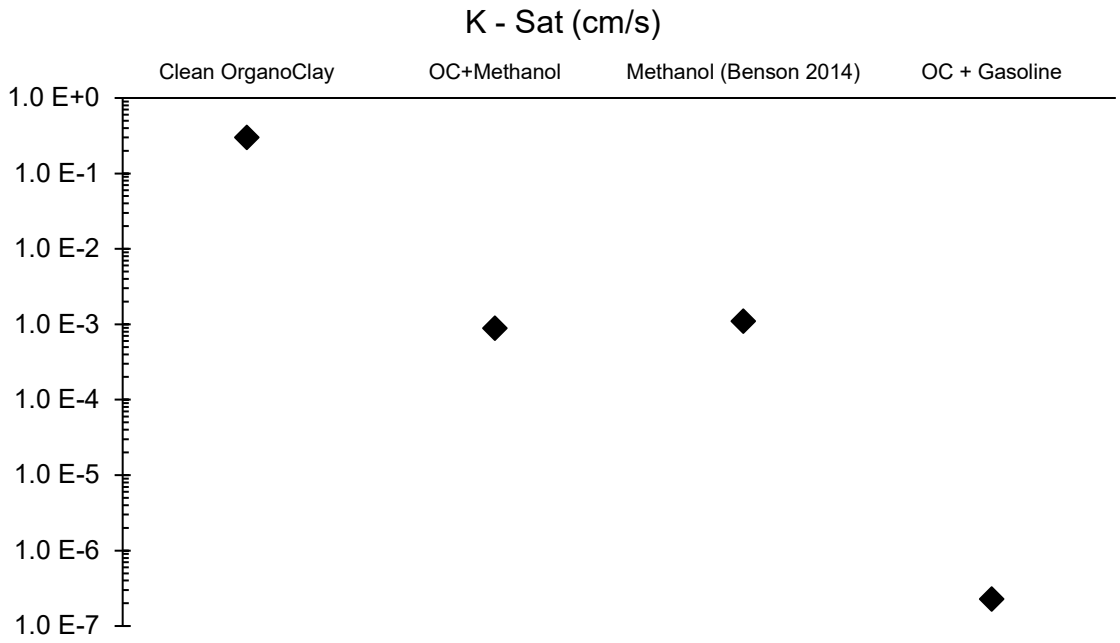


Figure 07: Saturated hydraulic conductivity of organoclay specimens. Similar test was performed by Benson (2014) on organoclay samples contaminated with methanol and other organic liquids.

4.2. Water Retention Curve (WRC)

The water retention curves the organoclay samples are shown in Fig. 08. The void ratio and the water content of a saturated soil bear a fixed relationship by the specific gravity of the soil. At the beginning of the test the samples are fully saturated and the saturated volumetric water content (θ_s) is calculated by measuring the void ratio of each sample based on the $wG_s = eS_r$, where w is the water content and G_s is the specific gravity which for organoclay is much lower than typical soil (clean OC $G_s = 1.4$) and e is the void ratio and S_r is the saturation which in the beginning of the test equals to one. Therefore by knowing exact amount of water in each sample and the volume of the entire sample we calculate the saturated volumetric water content (θ_s). $\theta_s$of the clean organoclay, contaminated with methanol and unleaded gasoline was 0.61, 0.42 and 0.09 in order. Sample that was contaminated with unleaded gasoline had the lowest saturated volumetric water content with the strongest organoclay reaction. The void spaces in this sample are reduced to such a degree that there is very little space left for water to saturate, effectively reducing the permeability and hydraulic conductivity.

The air entry (Ψ_A) is determined by drawing two tangent lines on the straight section of the water retention curve before and after the falling area. The air entry (Ψ_A) is known as the suction value where air penetrates through the pores of the specimen. The higher the air entry (Ψ_A) the lower the hydraulic conductivity and permeability of the sample. As reacted with NAPL, the air entry (Ψ_A) increased. The average air entry (Ψ_A) of the clean organoclay, contaminated with methanol and unleaded gasoline was 0.6, 2.0 and 22.0 kPa in order.

The average residual volumetric water content (θ_r) is calculated from θ_s by measuring the exact amount of water than exits each sample and reducing it from the total water

in the saturated state. θ_r at the end of the test for the clean organoclay, contaminated with methanol and unleaded gasoline was 0.22, 0.12 and 0.05 in order. The WRCs acquired from the three samples are according to expectations made after the saturated hydraulic tests. Organoclay has the highest reaction with unleaded gasoline, resulting in very low void spaces and permeability. The same can be observed in the WRC of this sample with the low θ_s and θ_r value and a high Ψ_A.

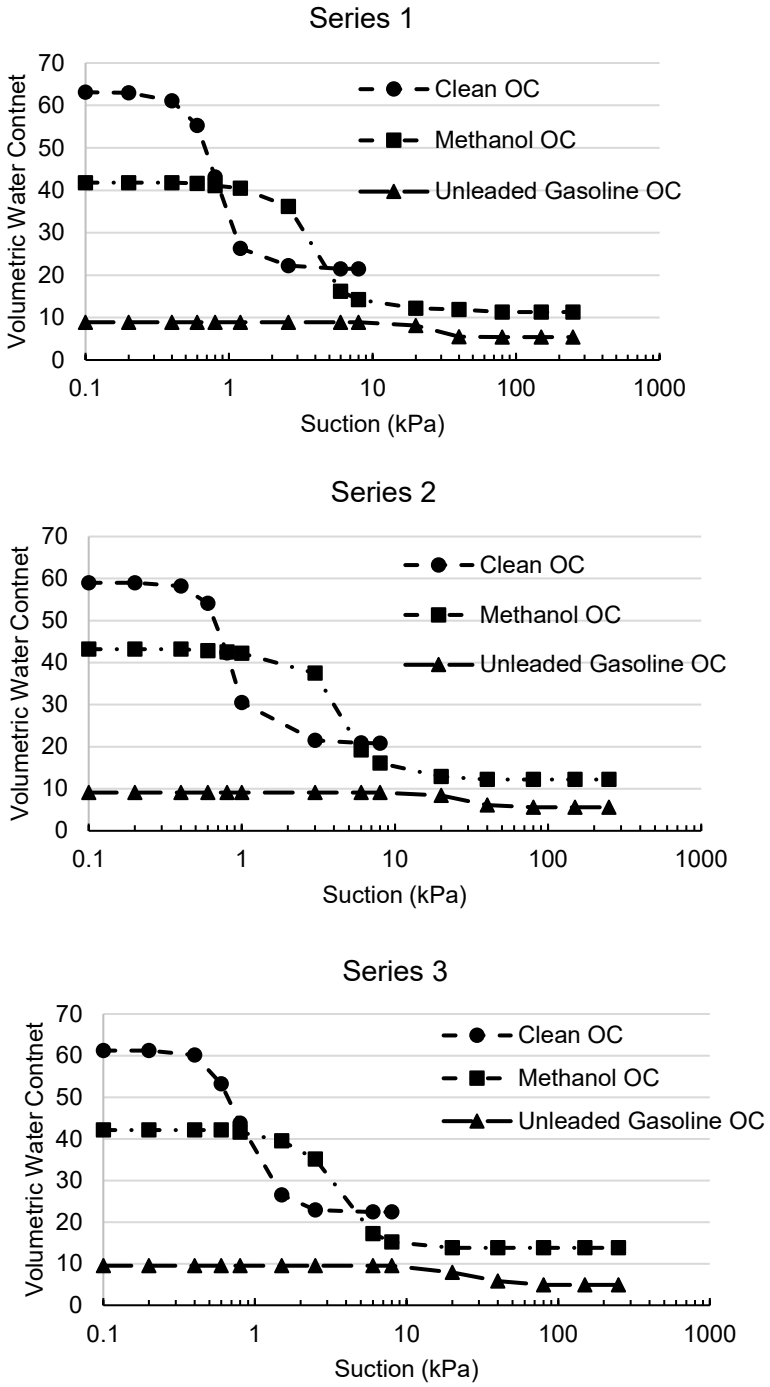


Figure 08: The water retention curve of clean organoclay and two organoclay samples contaminated with methanol and gasoline repeated three times (series 1, 2 and 3). Before 8 kPa the test is performed using the hanging column and afterwards the two contaminated samples are moved to the pressure plate to apply higher suctions.

4.3. Unsaturated Behavior Modeling of Organoclay Samples

The Brooks-Corey and van Genuchten models were used to fit the WRC data of the organoclay specimens. The model parameters are presented in Table 03. The van Genuchten model provided a better fit to the WRC data with lower mean squared error (MSE) values. The MSE values are presented in Table 04. The fitted WRC data using van Genuchten and Brook-Corey models are shown in Figs. 09 and10.

The unsaturated hydraulic conductivity changes throughout the test starting from its highest values, the saturated hydraulic conductivity and dropping down as suction increases. $k\ vs\ \Psi$ is an important figure derived from the WRC data using the fitting models. The hydraulic conductivity of organoclay samples are shown in Figs. 11 and12. As expected hydraulic conductivity drops dramatically as air enters the samples with the unleaded gasoline organoclay sample exhibiting the lowest permeability. The unsaturated hydraulic conductivity in BC and vG models are far apart (magnitude of 10^6) and the reason is the pore interaction parameters not being suitable for organoclay. The $p = 2$ and $l = 0.5$, pore interaction parameters, values used to calculate the hydraulic conductivity are common for soil and from Figs. 11 and 12 it is clear that cannot be used for organoclay. The hydraulic conductivity must be calculated during the WRC testing and then fitted to BC and vG models to find the pore interaction parameters suitable for organoclays.

Table 03: WRC fitting parameters using van Genuchten and Brooks-Corey models

Fitting Model	**Parameters**	**Clean OC**			**Methanol OC**			**Unleaded Gasoline OC**		
Test Series		**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Brooks-Corey	Ψ_a	0.70	0.65	0.64	3.50	3.40	3.20	23.00	23.50	23.00
	λ	4.62	2.98	2.69	3.21	2.54	3.35	6.43	3.68	3.01
van Genuchten	α	1.31	1.25	1.30	0.29	0.25	0.34	0.04	0.04	0.05
	n	5.35	6.17	4.37	3.97	4.10	3.87	7.42	5.04	3.65

Table 04: Average Mean squared error (MSE) values for van Genuchten and Brooks-Corey models to fit the WRCs of organoclay samples.

Fitting Model	Clean OC	Methanol OC	Unleaded Gasoline OC	MSE Average
Brooks-Corey	1.17E-01	1.78E-01	1.35E-03	9.88E-02
van Genuchten	3.53E-02	7.39E-03	5.15E-05	1.43E-02

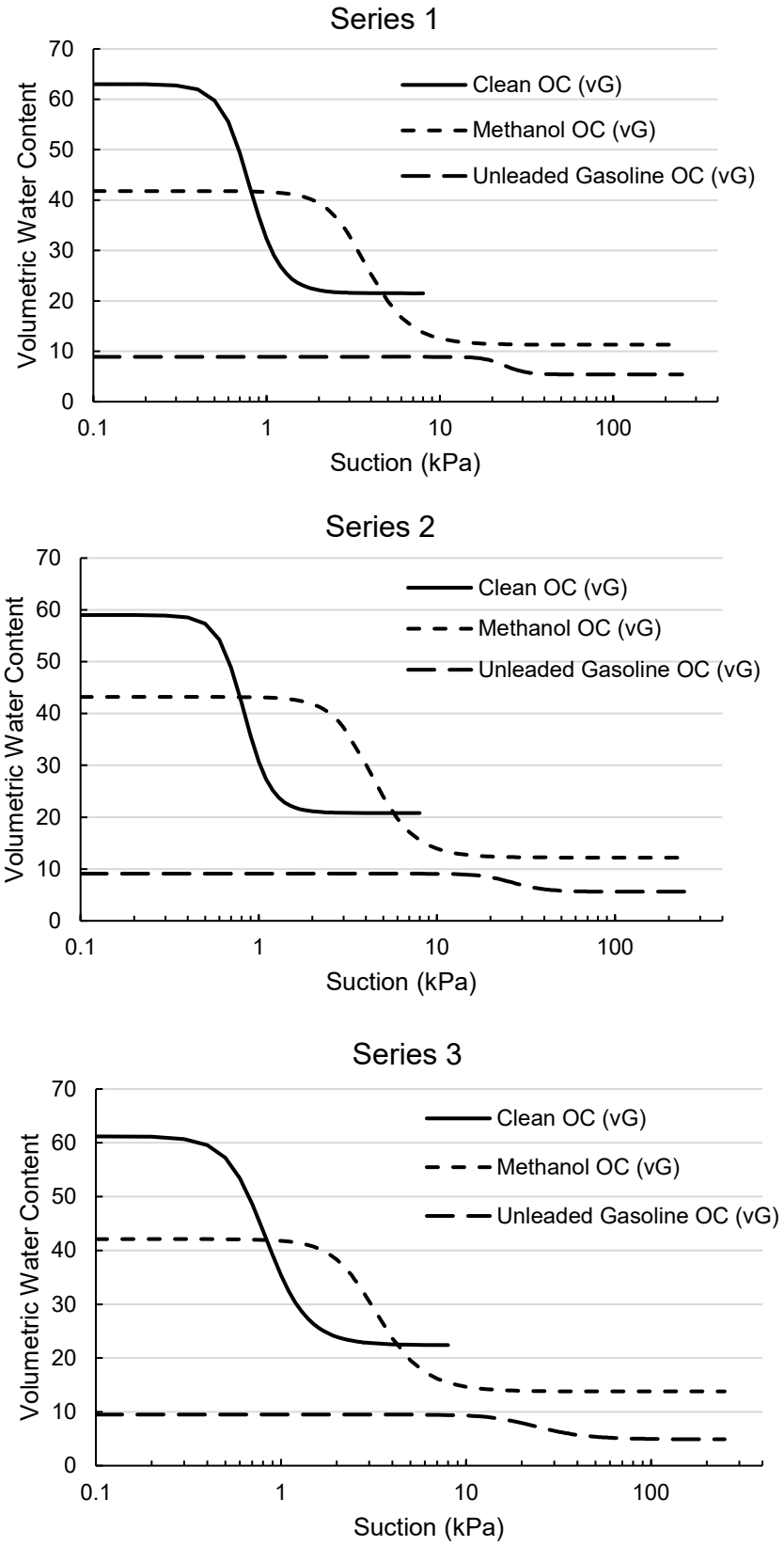


Figure 09: van Genuchten fit to WRC data using minimization of mean squared error (MSE)

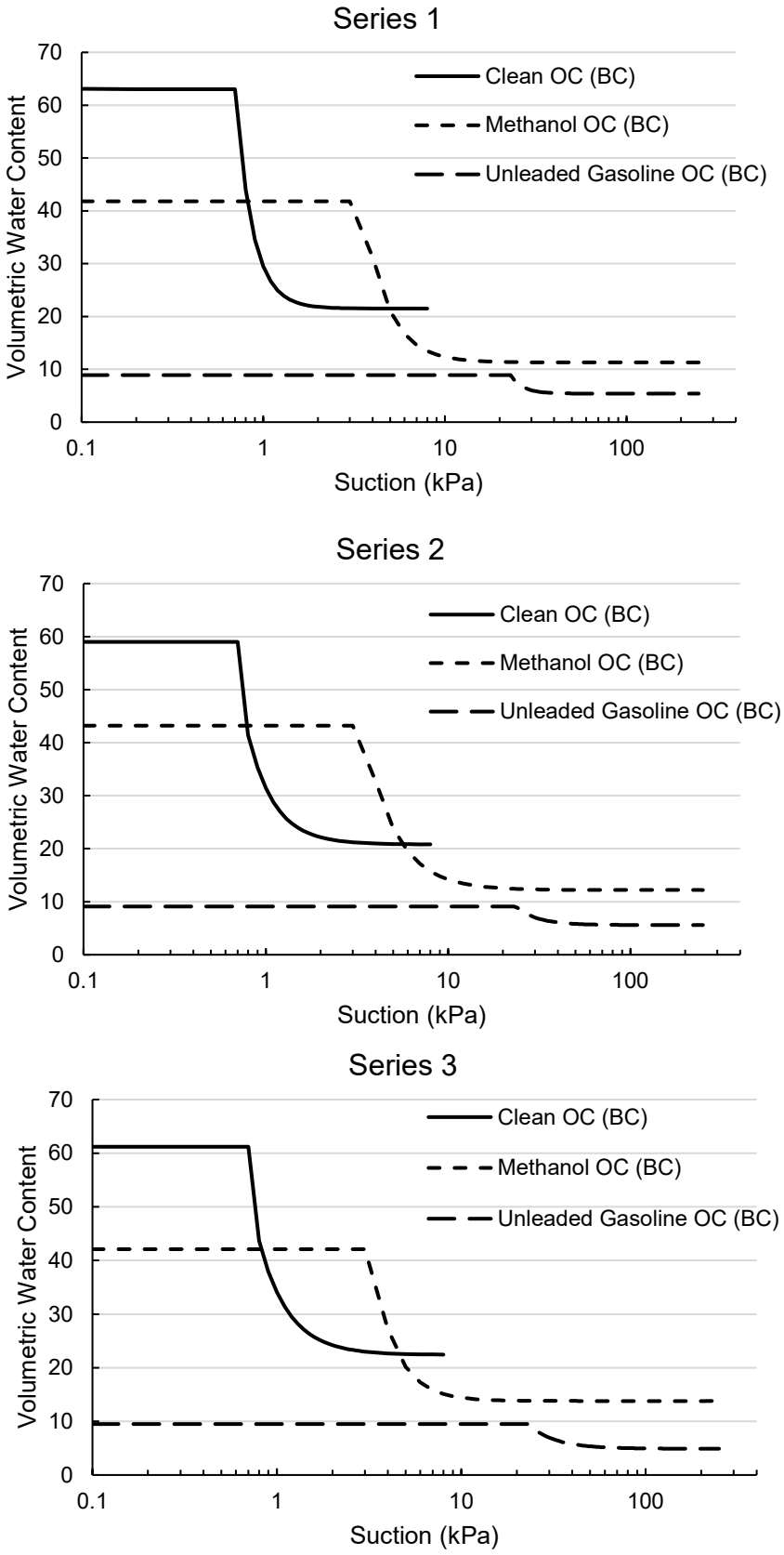


Figure 10: Brooks-Corey fit to WRC data using minimization of mean squared error (MSE)

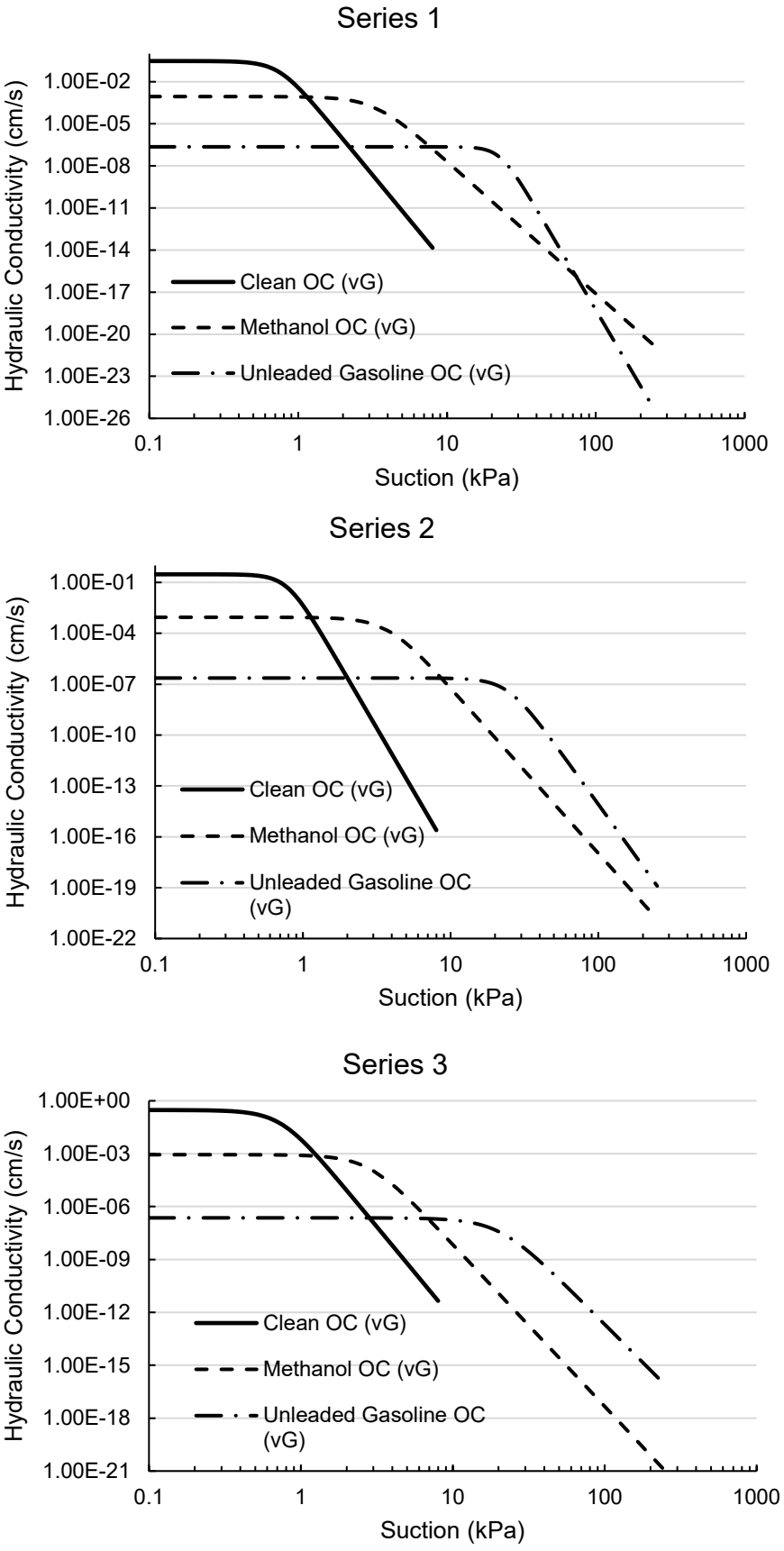


Figure 11: Hydraulic conductivity versus suction of organoclays samples by fitting van Genuchten model.

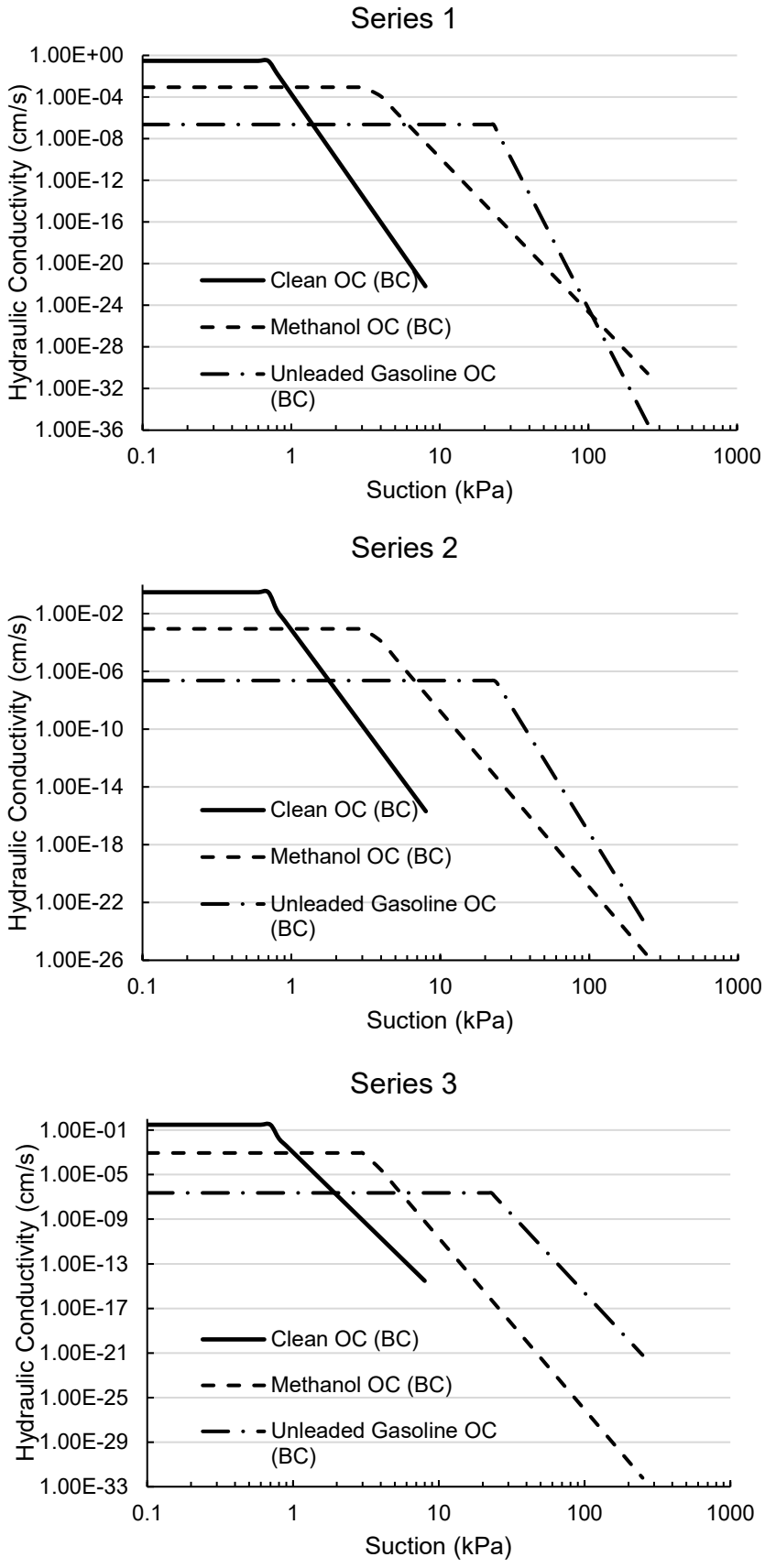


Figure 12: Hydraulic conductivity versus suction of organoclays samples by fitting Brooks-Corey model.

4.4. X-Ray Diffraction

The mineral composition of the bentonite section of the samples are identified and summarized in Table 05. The smectite percentage in organoclay drops from 65 to 49 and 22 for methanol OC and unleaded gasoline respectively while there is not a significant change in other bentonite minerals. Smectite percentage directly effects the swelling and hydraulic behavior of any sample. This drop is smectite content is in accordance with the drop in the hydraulic conductivity of the organoclay samples as well as the WRC pattern. The software provided diffraction angle vs intensity of the three samples is displayed in Fig. 13. There are clear differences in the peaks and intensities between the three organoclay samples.

Table 05: Mineral composition of the bentonite section of the three OC samples (Clean OC, methanol OC and unleaded gasoline OC).

Specimen	Smectite	Quartz	Plagioclase Feldspar	Halite	Potassium Feldspar	Amorphous Compounds
Chemical formula	X.3·nH2O [(Al1.5Fe3+.2Mg.3) Si4O10(OH)2]⁻.3	SiO_2	$Na(AlSi_3O_8)$, $Ca(Al_2Si_2O_8)$	Na Cl	$KAlSi_3O_8$	N/A
Clean OC	**65**	13	11	7	3	4
Methanol OC	**49**	14	10	7	N/A	20
Unleaded gasoline OC	**22**	13	10	7	N/A	48

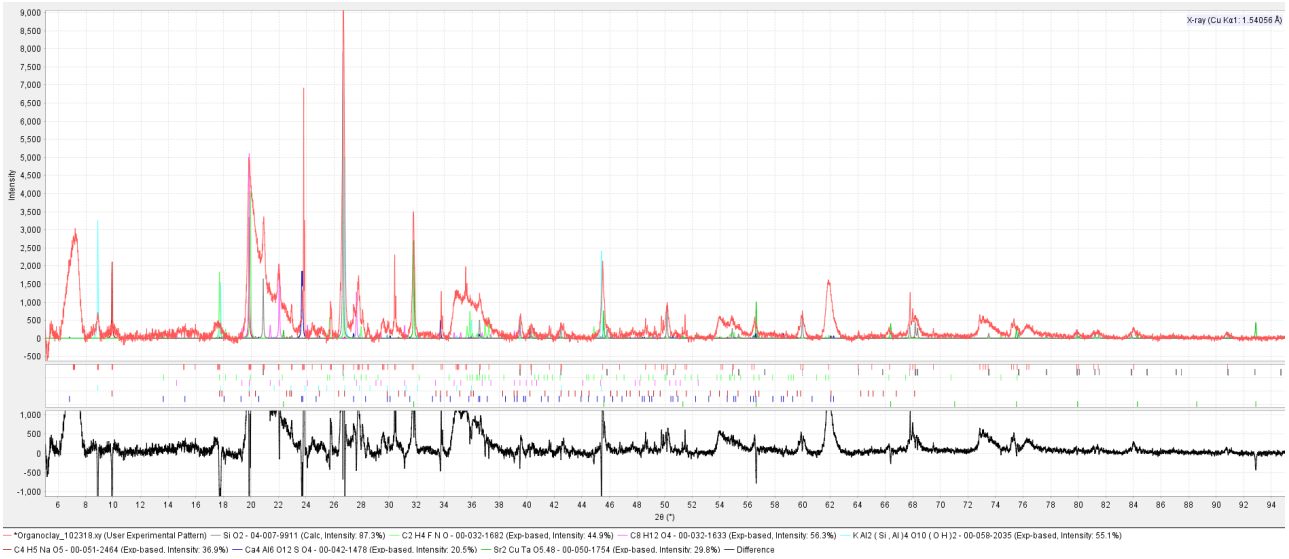


Figure 13: The diffraction angle vs intensity from the XRD test of the three organoclay samples (clean OC, methanol OC and gasoline OC) provided by the software for comparison.

4.5. Parameter Analysis

Based on the smectite percentages acquired from the XRD test we can conclude that smectite content can be represent degree of reaction with NAPL contaminant. Based on the relationship between smectite content and fitting model parameters organoclay specimens, the effect of the contaminant reaction on water retention behavior is displayed in Figs. 14 and 15. Figure 14 shows the relationship between van Genuchten's Parameters (α, n) and smectite content (%) for organoclay specimens. The 'α' parameter is related to the degradation of slope for the WRC. High NAPL reaction results in a lower α parameter. The relationship between Brooks-Corey's parameters (Ψ_a, λ) are presented in Fig. 15. Organoclays with lower smectite content account for higher reaction with NAPLs. Higher reaction results in a higher air entry in organoclay.

There is no specific pattern between 'n' and 'λ' parameters in relation to smectite content. Based on these figures no judgment can be made on pore size distribution of the media (λ, n).

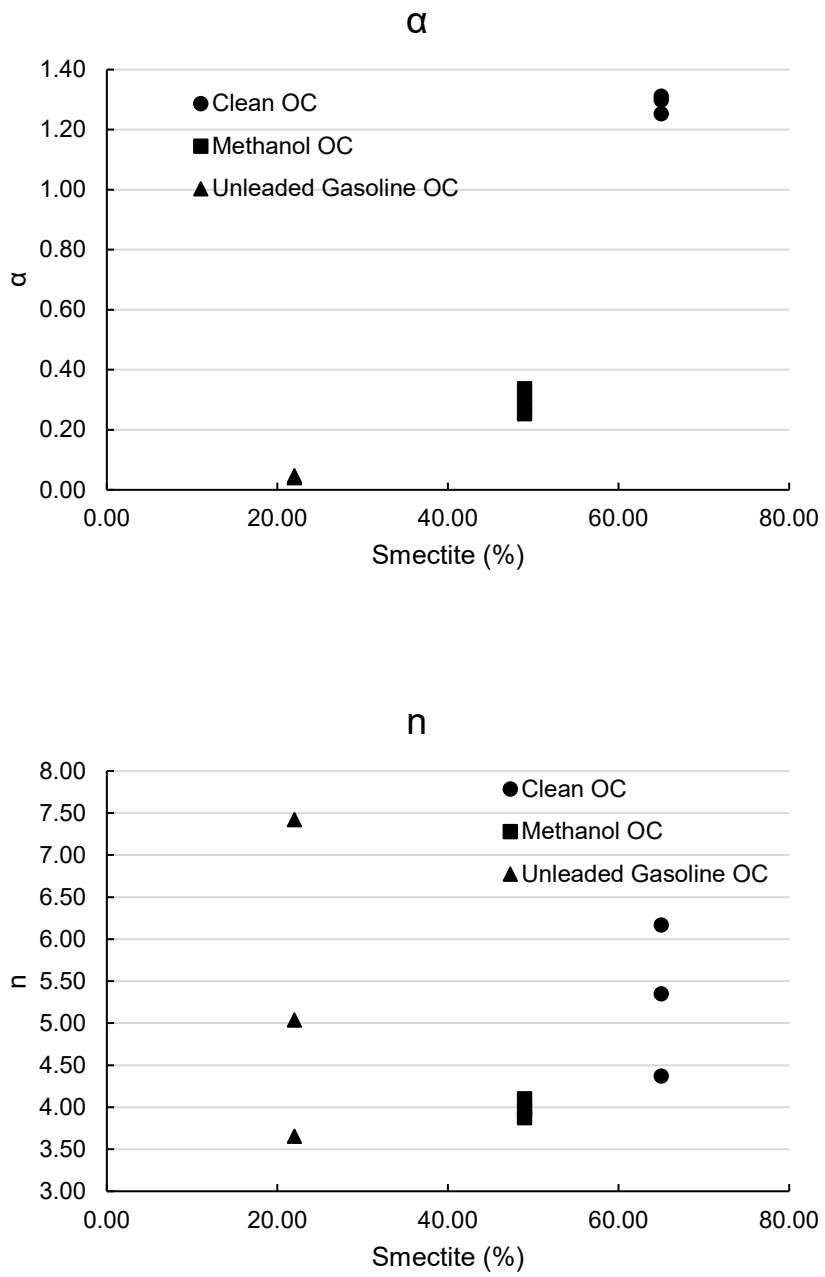


Figure 14: Relationship between van Genuchten parameters (α, n) and smectite content (%) for organoclay samples.

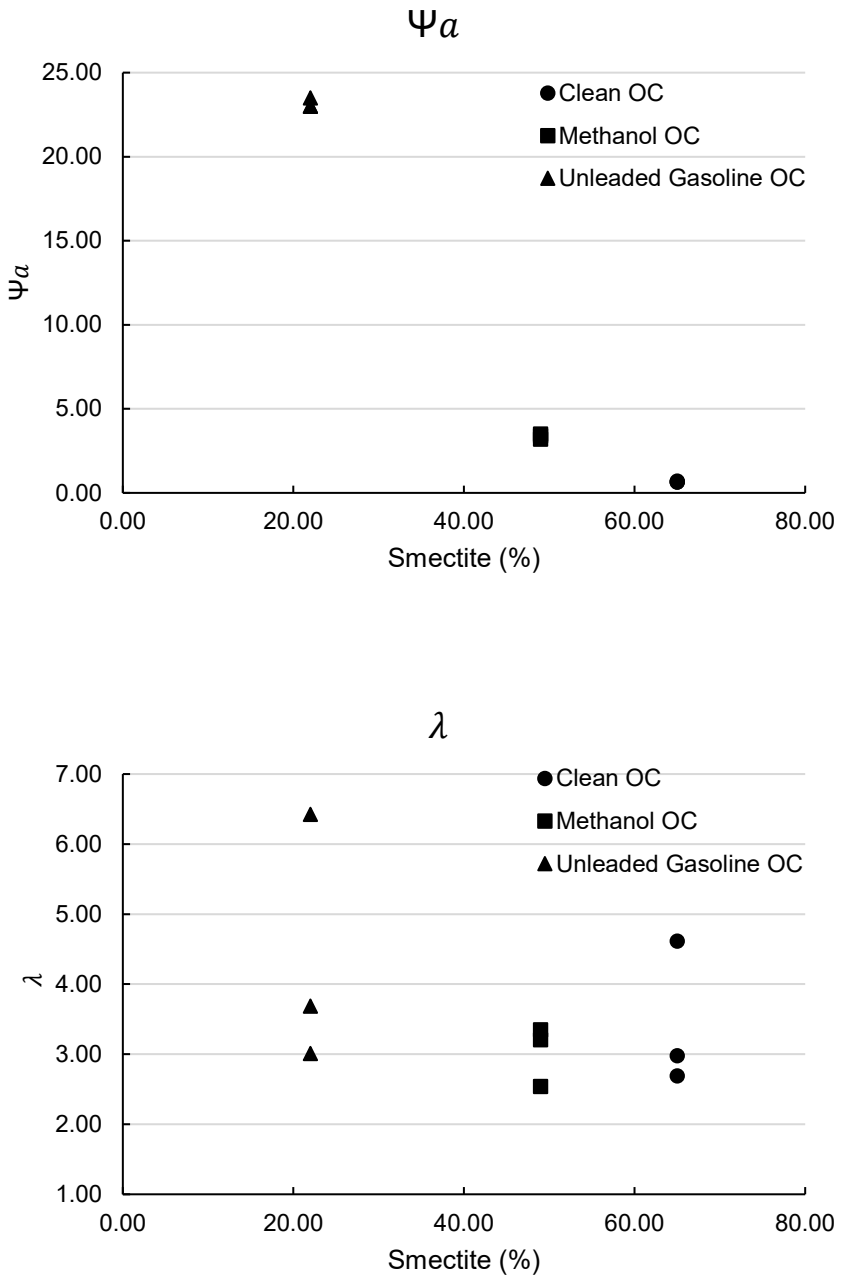


Figure 15: Relationship between Brooks-Corey parameters (Ψ_a, λ) and smectite content (%) for organoclay samples.

5. CONCLUSIONS

The tests performed on organoclay samples, used in reactive core mats to contain Non-Aqueous Phase Liquid (NAPL) contaminated sediments, were aimed to investigate and characterize mineralogical and hydraulic properties of organoclay before and after NAPL contamination.

Major findings of this study are:

- Mineralogical analysis shows a significant drop in smectite content before and after NAPL contamination. Smectite content reduces from 65% in clean organoclay to 49 % and 22% in organoclay samples contaminated with methanol and unleaded gasoline respectively. The change in content of other minerals present in the bentonite section (e.g., quartz, feldspar, and halite) of organoclay is negligible throughout the samples. Thus, smectite content is used as an indicator of NAPL reaction of organoclay.
- The degree of NAPL reaction in organoclay samples significantly effects its hydraulic properties. Clean organoclay has a high hydraulic conductivity of $3.0 \times 10^{-1}\ cm/s$. The saturated hydraulic conductivity drops to $8.8 \times 10^{-4}\ cm/s$ and $2.3 \times 10^{-7}\ cm/s$ after reaction with methanol and unleaded gasoline respectively. The organoclay sample contaminated with unleaded gasoline presents hydraulic conductivity values in the range of clay material and effectively displays how organoclay can be used as an impermeable layer to contain NAPL contaminated sediments after its reaction phase. The hydraulic conductivity of organoclay varied by approximately six orders of magnitude depending on the organic liquid used for contamination, with the lower hydraulic conductivity associated with the more highly refined fuel, unleaded gasoline,

composed of lighter distillates and ethylbenzene that induce greater swell, and the higher hydraulic conductivity with the hydrophilic liquid, methanol, that induce the least swell (or no swell).

- The higher the air entry (Ψ_A) the lower the hydraulic conductivity and permeability of the sample. As reacted with NAPL, the air entry (Ψ_A) increased. The average air entry (Ψ_A) of the clean organoclay, contaminated with methanol and unleaded gasoline was 0.6, 2.0 and 22.0 kPa in order.
- The average residual volumetric water content (θ_r) at the end of the test of the clean organoclay, contaminated with methanol and unleaded gasoline was 0.22, 0.12 and 0.05 in order.
- Brooks-Corey (1964) and van Genuchten (1980) models were used to fit the WRC data. Using the mean squared error (MSE) method, van Genuchten model provided a better fit.
- The unsaturated hydraulic conductivity was generated using the saturated hydraulic conductivity and Brooks-Corey (1964) and van Genuchten (1980) models. The $p = 2$ and $l = 0.5$, pore interaction parameters, values are commonly used for soil to calculate the unsaturated hydraulic conductivity. The results obtained from BC and vG models to not match in this regard suggesting that the interaction parameters cannot be used for organoclay. In order to find proper values for these parameters, the unsaturated hydraulic conductivity must manually be monitored and calculated during testing and then fitted to BC and vG models.
- As expected hydraulic conductivity drops dramatically as air enters the samples with the unleaded gasoline organoclay sample exhibiting the lowest permeability. The unsaturated hydraulic conductivity in BC and vG models are far apart

(magnitude of 10^6) and the reason is the pore interaction parameters not being suitable for organoclay.

- The trend of fitting parameters and smectite content and therefore degree of reaction, demonstrate unsaturated properties changing from coarse to finer WRC behavior.

The results in the study can be used for evaluating the unsaturated flow of NAPL through Reactive Core Mat (RCM) containing organoclay. This will be beneficial to the design and analysis of sediment capping systems consisting of RCM and cover soils.

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